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Comparison of bio-dissolution of spent Ni–Cd batteries by sewage sludge using ferrous ions and elemental sulfur as substrate

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Abstract

Bioleaching of spent Ni–Cd batteries using acidified sewage sludge was carried out in a continuous flow two-step leaching system including an acidifying reactor and a leaching reactor. Two systems operated about 30 d to achieve almost complete dissolution of heavy metals Ni, Cd and Co in four Ni–Cd batteries. Ferrous sulphate and elemental sulfur were used as two different substrates to culture indigenous thiobacilli in sewage sludge. pH and ORP of the acidifying reactor was stabilized around 2.3 and 334 mV for the iron-oxidizing system and 1.2 and 390 mV for the sulfur-oxidizing system. It was opposite to the acidifying reactor, the pH/ORP in the leaching reactor of the iron-oxidizing system was relatively lower/higher than that of the sulphur-oxidizing system in the first 17 d. The metal dissolution, in the first 12–16 d, was faster in the iron-oxidizing system than in the sulphur-oxidizing system due to the lower pH. In the iron-oxidizing system, the maximum solubilization of cadmium ($2500 \, \mathrm{mg \, l^{-1}}$) and cobalt ($260 \, \mathrm{mg \, l^{-1}}$) can be reached at day 6–8 and the most of metal nickel was leached in the first 16 d. But in the sulphur-oxidizing system there was a lag period of 4–8 d to reach the maximum solubilization of cadmium and cobalt. The maximum dissolution of nickel hydroxide ($1400 \, \mathrm{mg \, l^{-1}}$) and metallic nickel ($2300 \, \mathrm{mg \, l^{-1}}$) occurred at about day 12 and day 20, respectively.
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Keywords: Acidified sewage sludge; Spent Ni–Cd batteries; Ferrous sulphate; Elemental sulfur powder; pH and ORP; Metal dissolution

1. Introduction

With the improving awareness of environmental problems associated with spent dry batteries and electronic wastes, the methods to treat and recovery them are being developed. The traditional techniques are mainly pyrometallurgical process, hydrometallurgical process or the combination of the two (Bartolozzi et al., 1995; Chen, 2003; Qing and Jian, 2004; Freitas and Rosalém, 2005). Generally, biotechnology is a powerful and versatile alternative to chemical and physical methods for eluting the heavy metals associated with solids because of low demand for energy and materials, and low generation of waste and emissions (Chen and Lin, 2004).
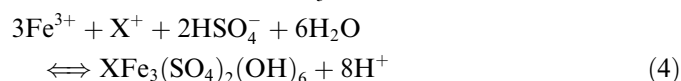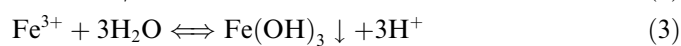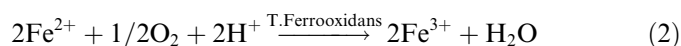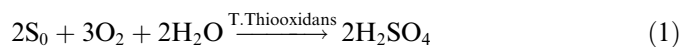
The microbial leaching process, using *Thiobacillus ferrooxidans* (an iron-oxidizing bacterium) and *Thiobacillus thiooxidans* (a sulfur-oxidizing bacterium) as the microorganisms or predominant microorganisms, has been developed and demonstrated to be an efficient, cost-effective means of removing heavy metals from sewage sludge (Lei et al., 2005). In the same way, bioleaching can be used to recover valuable metals from various metal-containing wastes such as electronic wastes or spent batteries (Solisio et al., 2002).

In this study, the dissolution of spent Ni–Cd batteries can be achieved either directly through the metabolism of bacteria or indirectly through the products of the microorganisms. Sewage sludge, as a substitute of pure microorganisms and culture were adopted because indigenous thiobacilli (mixed culture) is present in it as well as some nutriments such as N, P or K (Wen et al., 2003). The strains of thiobacilli mainly including *T. ferrooxidans*,

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T. thiooxidans and *Thiobacillus thioparus* (Chen and Lin, 2001a) can grow and produce sulphuric acid or ferric ions using elemental sulphur (Eq. (1)) or ferrous ions (Eqs. (2)–(4)) as the energy source with oxygen as the terminal electron acceptor and make the pH decrease substantially. A continuous pH decrease and ORP increase was observed, which was triggered by the oxidation of ferrous iron, either by a chemical or microbiologically mediated mechanism. Shifting of the pH towards acidic values results from the balance between the simultaneous consumption of protons in the oxidation of ferrous iron and the release of protons related to ferric iron precipitation.

$$2S_0 + 3O_2 + 2H_2O \xrightarrow{\text{T.Thiooxidans}} 2H_2SO_4 \tag{1}$$

$$2Fe^{2+} + 1/2O_2 + 2H^+ \xrightarrow{\text{T.Ferrooxidans}} 2Fe^{3+} + H_2O \tag{2}$$

$$Fe^{3+} + 3H_2O \Longleftrightarrow Fe(OH)_3 \downarrow + 3H^+ \tag{3}$$

$$3Fe^{3+} + X^+ + 2HSO_4^- + 6H_2O$$
$$\Longleftrightarrow XFe_3(SO_4)_2(OH)_6 + 8H^+ \tag{4}$$

Meanwhile a continuous flow two-step leaching system for the bioleaching of Ni–Cd batteries was constructed. It was mainly consisted of two reactors, the acidifying reactor and the leaching reactor. The acidifying reactor was used to culture iron- or sulfur-oxidizing bacteria in sewage sludge. Through a solid–liquid separation, the supernatant of the acidified sludge was used to leach metals from the scraps of the spent batteries in the leaching reactor. An advantage of this process is that the mixed consortium instead of the single bacteria (*T. ferrooxidans* or *T. thiooxidans*) to produce the sulphuric acid was applied. As in general bacteria growing within consortia may be involved in cross-feeding to reach optimal conditions for stability, therefore we decided to use consortia instead of pure cultures.

Because of its low costs, this process could be the first step in the treatment of nickel–cadmium batteries before recovering metals by physicochemical methodologies such as the co-precipitation to the ferrite.

Because different substrates added to the acidifying reactor can bring different dominant populations, different pH and ORP changes and the most important, the different medium for the dissolution of the heavy metals, the objectives of this study were to examine the leaching efficiency and dissolution behavior of Ni, Cd and Co in the electrodes of spent Ni–Cd batteries using the continuous flow two-step leaching system based on biohydrometallurgy with two different substrates: ferrous sulphate and elemental sulfur.

2. Experimental procedure

2.1. Sewage sludge sample

The sewage sludge used was concentrated mixture of primary (50% v/v) and secondary (50% v/v) sludge obtained from Minhang wastewater treatment plant in Shanghai, China. The sludge was adjusted to a moderate solids concentration to fit the process operation. The results of sludge analysis are presented in Table 1. The sample was kept at 4 °C before utilization.

2.2. Acclimation of iron- and sulfur-oxidizing microflora

The microorganisms used for the start-up of the system were obtained by acclimation of the indigenous iron-oxidizing bacteria or sulfur-oxidizing bacteria in sludge. A sample of 400 ml of sludge mixed with 1% (w/v) elemental sulphur powder was added to an Erlenmeyer flask, which was then incubated at 30 °C and 150 rpm in a gyratory shaker (Chen and Lin, 2001b; Seidel et al., 2006). After 12 d, the pH of sewage sludge dropped under 2.0 and the initial acclimation was completed. Subsequently, 80 ml of this acidified sludge was added to another 320 ml of the sludge sample with 1% (w/v) sulphur and re-incubated under the same conditions. This operation was repeated successively until the rate of pH reduction to 2.0 was maximized (2–3 d) over two consecutive transfers. It was assumed to be the final acidified sludge (pH 1.9–2.3) of sulfur-oxidizing microflora.

The acclimation of iron-oxidizing microflora was the same with the sulfur-one, except that the energy source was displaced by 4.0 g l^{-1} of Fe^{2+} (in the form of $FeSO_4 \cdot 7H_2O$).

2.3. Operation of the bioleaching process

The continuous flow two-step leaching system was mainly consisted of two reactors, the acidifying reactor and the leaching reactor with two settling tanks following them respectively (Fig. 1). The working volumes of the acidifying reactor and the leaching reactor were 4 l and 3 l respectively. The bacteria in the acidifying reactor were the indigenous acidophilic thiobacilli in sewage sludge and the culture was the sludge itself. The fresh sludge was continuously fed to the acidifying reactor, which operated at a

Table 1
Characteristics of the tested sludge

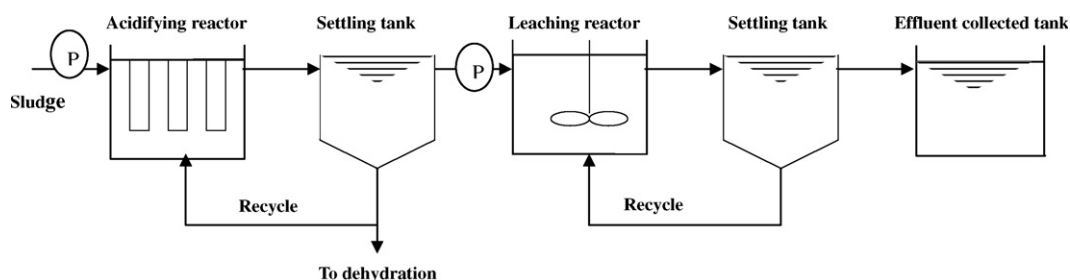| Parameters	Values
pH	6.31
Total solids (g l^{-1})	20.06
Volatile solids (g l^{-1})	10.8
Metals (mg kg^{-1} dry weight)	
Cd	5.0
Ni	28
Co	0.35
Fe	6534
Al	5621
Cu	102
Cr	39
Ca	20521
Zn	760
Pb	8.6
Mg	3003
Mn	214

Fig. 1. Schematic diagram of the metals leaching process.

Table 2
Summary of the total metals in one spent Ni–Cd battery (values are the average of 3 samples)

Battery materials	Average weight (g)	Elemental chemical composition (% w/w) of electrode materials					
		Ni	Cd	Co	Fe	Zn	K
Cathodic plaque	5.6132	41.7	1.6	5.1	0.1	1.9	3.6
Anodic electrode powder	5.1651	0.9	64.8	0.1	–	0.1	1.8
Steel support grid	0.8834	1.2	1.1	–	73.3	0.5	–
Fibrous separator	1.5162	0.06	0.02	0.01	–	–	0.07

fixed level with overflow going to the settling tank. In the first settling tank, 20% of the thickened sludge was recycled to the acidifying reactor to maintain the concentration of the active acidophilic thiobacilli. The supernatant from the settling tank was connected to the leaching reactor which contained anodic and cathodic materials obtained from nickel–cadmium batteries. The effluent containing high concentration of heavy metals was collected for the further recovering of Ni, Cd and Co.

Two suits of system operated synchronously with the same parameters except the substrates added to the acidifying reactor. At the start-up of the systems, 1 l of the final acidified sludge was transferred into the acidifying reactor then the fresh sewage sludge mixed with 1% (w/v) of elemental sulphur or 4.0 g l^{-1} FeSO$_4 \cdot$ 7H$_2$O was continuously fed to the acidifying reactor at 1.5 l d^{-1}, in which air was supplied with an air diffuser to provide carbon dioxide as the sole carbon source of the chemoautotrophic sulphur-oxidizing bacteria and ensure high level dissolved oxygen concentration (DO > 3.0 mg l^{-1}) as the electron acceptor. The aeration rate was 0.18–0.2 vvm (volume of air: vol of sludge in reactor: min) and the volume percent of CO$_2$ in air is 0.036% which is appropriate for the growth of thiobacilli (Filali-Meknassi et al., 2000).

The systems operated at ambient temperature of 25–35 °C (Tsai et al., 2003). The supernatant flowed into the leaching reactor was controlled at 1 l d^{-1}. The hydraulic retention time of the acidifying and leaching reactor was 2.2 d and 1 d, respectively. Keep the agitation 120 rpm in the two reactors with mechanical stirrers to ensure the complete mixing.

The type of the spent batteries treated were AA-sized Ni–Cd batteries from Shanghai Pinxin power resource industry, China. In the batch experiment of each system, four batteries were leached with the total weight of 13.178 g × 4 including the anode, cathode and electrolyte as well as a small quantity of additive material. Summary of the total metals in spent Ni–Cd batteries is presented in Table 2.

2.4. Analytic method

During the leaching process, the heavy metals (Ni, Cd and Co) concentration of the effluent solution was measured at 3 d interval by plasma emission spectrometry (ICP-AES, Iris Advantage 1000). The pH and ORP value in the two main reactors were determined each day using a pH meter in which a combined pH electrode and a combined Eh electrode which uses Ag/AgCl (sat) as reference electrode (Mettler Toledo 320-S). Phase composition of the disaggregated electrode materials was identified by X-ray power diffraction (XRD), the patterns being obtained with a Rigaku Geiserflex D/MAX-RC diffractometer (Cu Kα radiation), equipped with a curved crystal graphite monochromator and the following conditions, 50 kV, 80 mA and a scan speed 8° (2θ) min^{-1}.

3. Results and discussion

3.1. pH and ORP changes during the first step acclimation of microflora

The microorganisms used for the start-up of the system were obtained by acclimation of the indigenous iron-oxidizing bacteria or sulfur-oxidizing bacteria in sludge. The previous study of substrate amount added showed that 1% (w/v) S^0 (Wen et al., 2003) or 4 g l^{-1} FeSO$_4 \cdot$ 7H$_2$O (Chan et al., 2003) is preferred at this sludge solids concentration. For the substrate FeSO$_4 \cdot$ 7H$_2$O, too much ferric iron precipitates may inhibit bacterial iron oxidation due

to the formation of a layer of ferric iron precipitates on the bacteria, which hinders proton diffusion at pH above 2.5.

Fig. 2 is the comparison of pH and ORP changes during the first step of acclimation of microflora with substrate S^0 and $FeSO_4 \cdot 7H_2O$. A control sample was conducted with no substrate added. In the first 5 d, pH decreased faster with $FeSO_4 \cdot 7H_2O$ than with S^0 but in the latter half of the acclimation, the result was reversed and substrate S^0 make the final pH decreased to below 1.0. While the final pH of substrate $FeSO_4 \cdot 7H_2O$ was about 2.0. Generally, in the high pH range of 5.0–7.0, ferrous iron oxidation is mainly the result of the chemical oxidation which was relatively faster, below pH 5.0 the process is mainly related to bacterial catalysis (Meruane and Vargas, 2003).

The final pH of the sludge by elemental sulfur can be reduced to 1.0 from an initial pH of 6.0–7.0 of the fresh sludge, which indicated that the *Acidithiobacillus thiooxidans* in the sludge have a wide adaptability of pH. It was considered that in sewage sludge there are two species of sulphur-oxidizing bacteria including less-acidophilic and acidophilic thiobacilli. In the acclimation of sulfur-oxidizing microflora, a lag in pH decrease from 6.0–7.0 to 5.0 was observed. The acidification takes place in two steps:
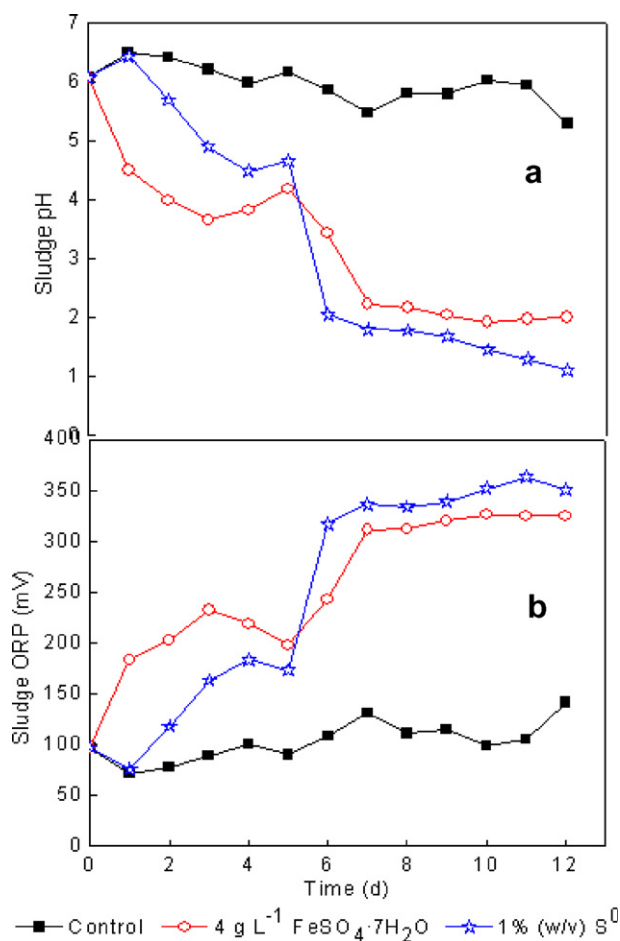
an initial decrease in pH from 7.0 to 4.0–5.0 by less-acidophilic thiobacilli followed by a lag in bacterial growth and a further pH reduction from 4.0–5.0 to 2.0 or below by the acidophilic thiobacilli (Shen et al., 2002).

3.2. Sludge acidification in the acidifying reactor

The process in this experiment was a continuous flow two-step leaching system, in which the growth of the microorganisms and the leaching of the batteries were separated to avoid the toxicity of the heavy metals to the bacteria (Brandl et al., 2001).

Fig. 3 presents the pH and ORP in the acidifying and leaching reactor during the 30 d operation. It can be seen that the pH and ORP in the acidifying reactor was relatively steady. pH stabilized around 2.3 in the iron-oxidizing system and 1.2 in the sulfur-oxidizing system. The corresponding ORP of the two systems was operating at 317–334 mV and 320–390 mV respectively due to the enrichment of the acidophilic thiobacilli which caused the

Fig. 2. pH (a) and ORP (b) changes during the first step acclimation of microflora with substrate S^0 and $FeSO_4 \cdot 7H_2O$ (a control sample was conducted with no substrate added).
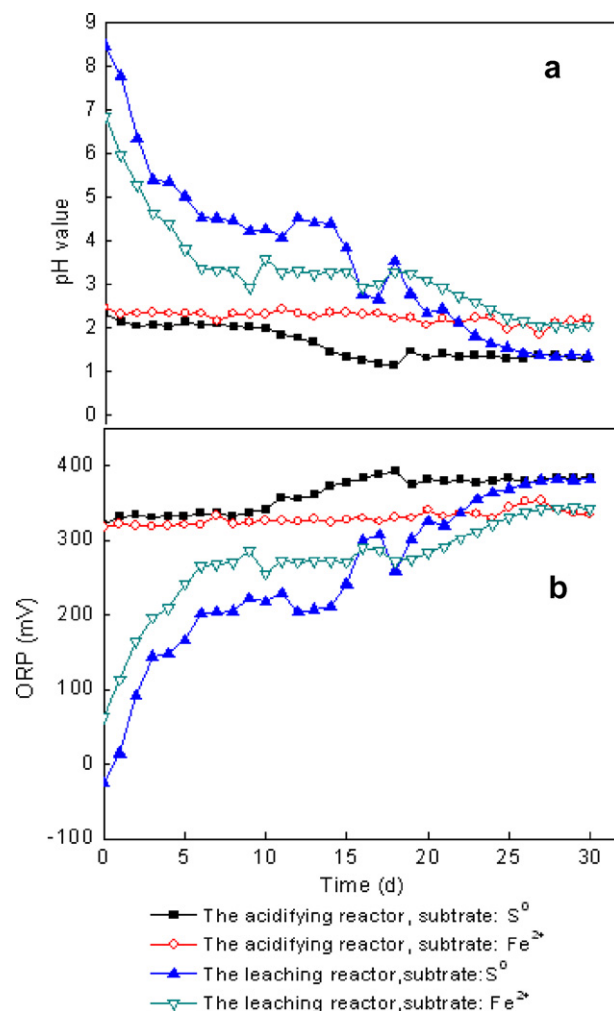
Fig. 3. pH (a) and ORP (b) in the acidifying reactor and the leaching reactor with different substrates.

oxidation of Fe(II) to Fe(III) or sulfur to sulfate resulting in a decrease in the free electrons concentration (Couillard et al., 1994; Chartier and Couillard, 1997).

In the usual bioleaching process with $FeSO_4 \cdot 7H_2O$ as the energy source, the major disadvantage is the requirement of the addition of acid for pH adjustment because *T. ferrooxidans* grows at pH 4.5 or below (Wong et al., 2002). But in the continuous culture process the fresh sludge flowing into the acidifying reactor did not need the pre-acidification because the pH maintained relatively low. However, in the iron-oxidizing system, the final pH was difficult to be reduced to under 2.2. The oxidization of the ferrous iron to ferric iron by the microorganisms is acid-consuming (Eq. (2)) whereas ferric iron is almost insoluble at a neutral pH and the forms of $Fe(OH)_3$ precipitation are acid-producing reaction. And also the precipitation of ferric phosphate is possible because a large quantity of phosphate is present in the sludge (Blais et al., 1993). When the pH is lower than 2.2, Eqs. (3) and (4) would happen reversely (Xiang et al., 2000). Furthermore, the strong acidity (<1.3) inhibits the activity of *T. ferrooxidans*.

3.3. pH and ORP changes with time in the leaching reactor

pH and ORP changes with time in the leaching reactor are also presented in Fig. 3. Due to the effect of alkaline electrolyte in the scraps of the spent Ni–Cd batteries, an increase of the initial pH and decrease of the ORP appeared. In the two systems, pH increased sharply from about 2.2 to the 7.0–8.5 and ORP decreased sharply from 330 mV to lower than 50 mV when the supernatant from the settling tank was conducted into the leaching reactor. With the continuous flowing of the fresh bio-sulphuric acid to the leaching reactor and the discharging of the effluent, the pH and ORP decreased and increased respectively with time. At the end of the 30 d operation, the pH and ORP of the liquid effluent from the leaching reactor was the same as the influent, so did the heavy metal concentration.

But it was opposite to in the acidifying reactor, the pH/ORP in the leaching reactor of the iron-oxidizing system was relatively lower/higher than that of the sulphur-oxidizing system in the first 17 d. In the iron-oxidizing system, Eqs. (3) and (4) were progressed resulting from the proton consumptions largely when the supernatant was connected to the leaching reactor. And then the protons can be reproduced. It can be said to some extent that the iron-oxidizing system has a stronger buffering capacity of pH than the sulphur-oxidizing system due to the vast presence of Fe(III) and the mutual transformation with Fe(II).

To sum up, the iron-oxidizing bacteria together with the addition of iron sulfate caused a stronger oxidizing environment through the production of Fe(III) for the leaching of some reductive metals than the sulfur-oxidizing bacteria. However, the acid generation capacity of the sulfur-oxidizing system was higher than that of the iron-oxidizing system resulting in a lower final pH and a higher removal of some pH-dependent metals with low solubility.

3.4. Metal solubilization in the leaching reactor

Fig. 4 shows the change of nickel, cadmium and cobalt concentration in the effluent during the bioleaching process with different substrates. When the metal concentration of the effluent was equal to that of the influent of the leaching reactor (the leached metals from the sludge), it was assumed that the electrode metals were completely leached. Table 3 is the summary of the results of total metals dissolution with different substrates. The metal recovery can be
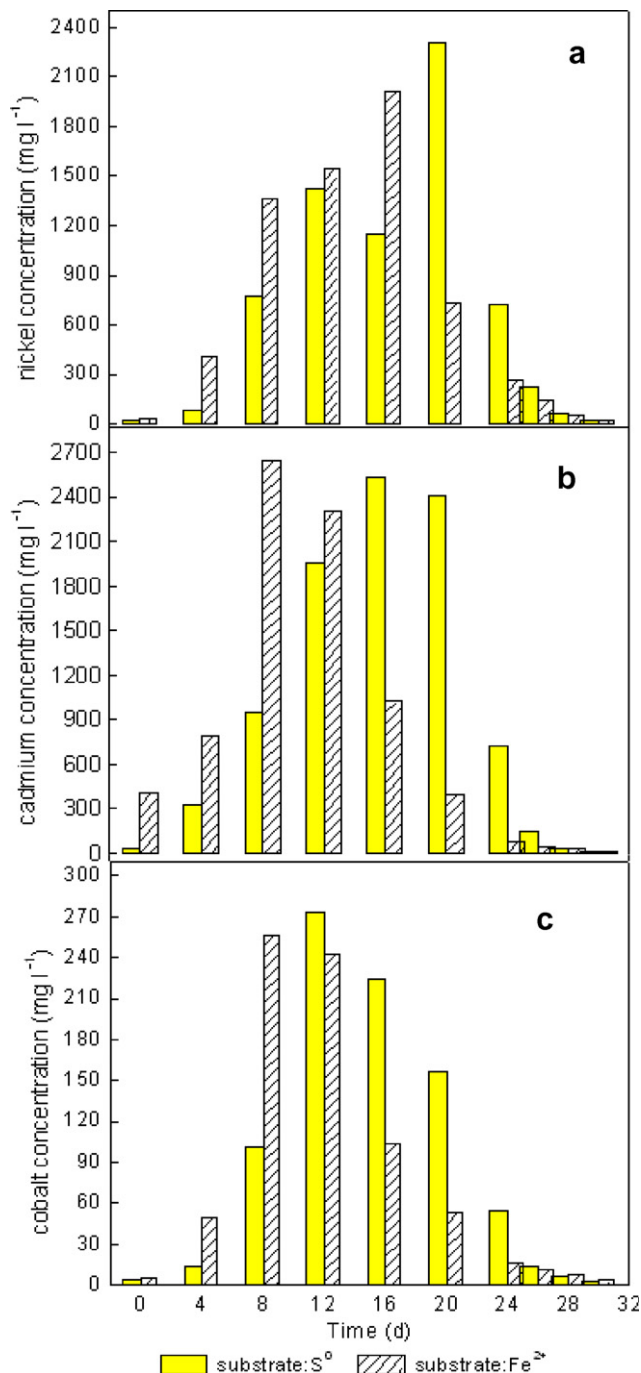
Fig. 4. Change of nickel (a), cadmium (b) and cobalt (c) concentration in the effluent during bioleaching process with different substrates.

Table 3
Summary of the results of total metals dissolution with different substrates

Substrate	Metals concentration of collected leachate (mg l^{-1})			Contribution of sludge (mg l^{-1})[a]			Total collected leachate (l)
	Ni	Cd	Co	Ni	Cd	Co	
Ferrous ion	327.29	449.98	33.77	0.67	0.09	0.0071	30
Elemental sulfur	320.12	453.67	38.79	0.73	0.11	0.0082	30

[a] Data determined from the average concentration of the acid supernatant flowing into the leaching reactor.

calculated from comparison of the ingoing metals in Table 2 and the outgoing metals in Table 3. For Cd a 99% recovery was reached, while for Ni and Co it came to 100% recovery in 30 d leaching.

As can be seen from Figs. 4 and 3, pH appeared to be the major factor responsible for the solubilization of Ni, Cd and Co. From the beginning to about 12–16 d, the concentration of the three metals in effluent was higher in the iron-oxidizing system than in the sulphur-oxidizing system due to the lower pH. In the iron-oxidizing system, the maximum solubilization of cadmium (2500 mg l^{-1}) and cobalt (260 mg l^{-1}) can be reached at day 6–8 and the corresponding pH was 3.0–3.5. But there was a lag period of 4–8 d to reach the maximum in the sulphur-oxidizing system. Thus the iron-oxidizing system is more efficient in view of its shorter bioleaching time and will be more suitable for plants receiving high loading rate. However, the sulphur-oxidizing system has a stronger acid generation capacity being more suitable for a long time leaching.

The most of metal cadmium was leached in the maximum dissolution days till the end of the leaching. But for the metal cobalt a gradual decrease followed the maximum dissolution because cobalt is usually added to nickel during the manufacturing process of the positive electrodes and probably it was co-precipitated as solid solution, being part of the Ni(OH)$_2$ structure.

The pattern of nickel solubilization differed from that of cadmium and cobalt in hydroxide from which was mostly solubilised at higher pH values. In the case of nickel, the leaching of nickel hydroxide and nickel in metallic form (Ni^0) was obtained separately since the leaching of these species occurs sequentially at different acidity levels (Nogueira and Margarido, 2004). The phenomenon was obvious in the sulphur-oxidizing system. Fig. 5 presents the XRD patterns of the initial cathode material of spent Ni–Cd battery (a), the initial anode material (b) and cathode solid residue after 20 d bioleaching with the substrate elemental sulfur (c). Due to the anode material is farinose so the residue can not be obtained after bioleaching. It can be seen that after 20 d leaching, only metallic Ni presented in the solid residue of the cathode.

From Fig. 4a we can see that the maximum dissolution of nickel hydroxide (1400 mg l^{-1}) and metallic nickel (2300 mg l^{-1}) occurred at about day 12 with the pH value 4.0 and day 20 with the pH value 2.5 respectively. When FeSO$_4 \cdot$ 7H$_2$O was used as the substrate, in the first 16 d the most of metal nickel was leached in the pH of 2.5–3.0. Nickel released more slowly than cadmium did. It
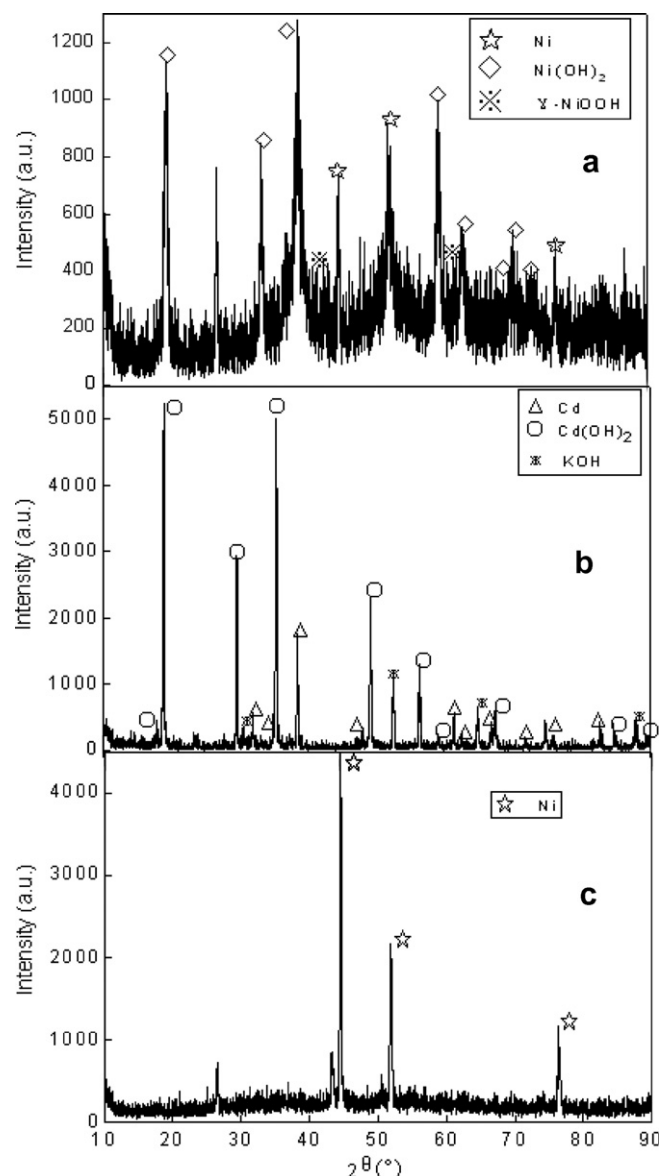

Fig. 5. XRD patterns of the initial cathode material of spent Ni–Cd battery (a), the initial anode material (b) and cathode solid residue after 20 d bioleaching with the substrate elemental sulfur (c).

may be due to the higher solubility of cadmium hydroxide than nickel hydroxide and the higher reducing power of cadmium than nickel, i.e. elemental cadmium is more easily oxidized than elemental nickel (Cerruti et al., 1998). The attack of cadmium by bacteria was faster than that corresponding to nickel.

Besides the acid dissolution of the metals, another possible mechanism accelerating the leaching of the electrodes of spent batteries is galvanic interactions, which is quite often the case in natural ores (Berry et al., 1978; Mehta and Murr, 1983; Natarajan and Iwasaki, 1983). In the interaction, the metal oxide with the higher electrode potential becomes a cathode and corrodes (oxidizes) the one with the lower potential becoming anode. In the leaching reactor, the following species existed in the mixture: $Ni(OH)_2$, $NiOOH$, $Cd(OH)_2$ and the metallic Ni, Cd, Co (Chen, 2003; Pietrelli et al., 2005). Due to the vast presence of Fe^{3+}/Fe^{2+} redox couple which has a very positive standard electrode potential (+770 mV at pH 2.0) in the iron-oxidizing system, the ''mineral'' with the lowest potential always had the highest extent of microbial colonization and of weathering (Tributsch and Rojas-Chapana, 2000; Rawlings, 2005).

4. Conclusions

The research demonstrated a new method that using acidified sewage sludge to remove the heavy metals in spent Ni–Cd batteries and a continuous flow two-step leaching system was introduced. It was an effective process that can achieve complete leaching of heavy metals Ni, Cd and Co in spent Ni–Cd batteries in enough time. The toxicity of the heavy metals to the bacteria was avoided and the sludge did not need the preacidification when $FeSO_4 \cdot 7H_2O$ was used as the substrate.

In the acidifying reactor the final pH with substrate sulphur ($\sim$1.2) was lower than with substrate $FeSO_4 \cdot 7H_2O$ ($\sim$2.2) due to that $Fe(OH)_3$ precipitation can not exist at pH lower than 2.2. But when the supernatant was connected to the leaching reactor the pH was higher in the sulphur-oxidizing system which resulted in the slower dissolution of the metals. The ORP presented the reverse trend with the pH.

pH appeared to be the major factor responsible for the solubilization of Ni, Cd and Co. Thus the iron-oxidizing system is more efficient in view of its shorter bioleaching time and will be more suitable for plants receiving high loading rate. However, the sulphur-oxidizing system has a stronger acid generation capacity being more suitable for a long time leaching.

Cadmium hydroxide, elemental cadmium and cobalt were more easily leached than nickel hydroxide and metallic nickel in both systems due to the higher solubility of cadmium hydroxide than nickel hydroxide and the higher reducing power of cadmium than nickel.

Acknowledgements

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